

Electrical conductivity of air-exposed and unexposed lead selenide thin films: Temperature and size effects

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Thin films of PbSe of different thicknesses have been prepared on glass substrates at room temperature by vacuum deposition. It is found that the electrical resistivity of the air-exposed films is much higher (by about 2 to 3 orders) than that of the as-grown (unexposed) thin films. The electrical resistivity temperature behaviors of both the air-exposed and as-grown (unexposed) thin films of PbSe are different. These observations can be explained by considering that the desorption of adsorbed gas molecules (mainly oxygen) and creation of defects at higher temperatures during heating influence the electrical conduction. The as-grown (unexposed) thin-film conductivity exhibits the expected reciprocal thickness dependence due to thickness effects, but the air-exposed film conductivity does not. This can be explained as due to the complete masking of the thickness effect by the gas-adsorption effect in air-exposed film conductivity. The reciprocal thickness dependence observed in the case of unexposed-film conductivity has been explained by the "effective mean free path" model. The mean free path l_g and the specular parameter p are determined as 580 Å and 0.9, respectively.

I. INTRODUCTION

Electrical-conductivity studies on lead chalcogenides have been carried out by many workers both in low- and high-temperature ranges on films as well as on bulk.¹⁻⁸ The bulk carrier concentration reported in the literature is $3 \times 10^{16} \text{ cm}^{-3}$ for PbSe.^{9,10} The minimum direct energy gap E_g at room temperature has been quoted as 0.29 eV. Zemel *et al.*¹¹ reported time-dependent behavior of electrical properties in PbSe films. Annealed films of PbS showed a decrease in mobility when measured after one day, but no considerable change in Hall constant was observed. The energy gap values reported were 0.31, 0.27, and 0.41 eV for PbTe, PbSe, and PbS films, respectively. At 77 K, these values were 0.20, 0.15, and 0.28 eV, respectively. The carrier concentrations reported were 2×10^{18} , 3×10^{18} , and $2 \times 10^{18} \text{ cm}^{-3}$, respectively.

Our present work on the conductivity of PbSe films mainly deals with the analysis of the temperature and thickness dependence of conductivity of both "as-grown" and "air-exposed" films. The conductivities in the two cases were found to be considerably different due to the gas-adsorption effects. A qualitative explanation for the temperature dependence of conductivity of PbSe films, both as-grown and air-exposed films, has been given. The thickness dependence of conductivity of as-grown films of PbSe is analyzed on the basis of the "effective mean free path model" suggested by Tellier *et al.*¹² However, the variation of the exposed-film conductivity with thickness was found to be quite random.

II. EXPERIMENT

PbSe films of different thicknesses were prepared by thermal evaporation of PbSe bulk alloy onto clean glass substrates held vertically above the evaporation source at

room temperature in a pressure of 5×10^{-5} Torr. The bulk Pb-Se alloy used for film preparation was prepared in the laboratory by vacuum sealing and heating a stoichiometric mixture (1:1 ratio) of Pb and Se of purity 99.999% (Nuclear Fuel Complex, Hyderabad, India).

In each film preparation, a given quantity of the bulk alloy was taken in the boat and it was completely evaporated at a very high rate. Films of different thicknesses were prepared in individual, separate evaporations. The reason for adopting this method of film preparation was to (i) avoid fractionation of the alloy in a single evaporation (by employing a very fast rate of evaporation so that the components evaporate almost at the same rate) and (ii) avoid using the left-over alloy from an earlier evaporation for a subsequent evaporation to prepare another film, because the left-over alloy may have a changed composition (due to preferential evaporation of one of the components, for example Se) from that of the original alloy. The glass substrates used for the film preparation were cleaned using warm chromic acid, Teepol detergent, and isopropyl alcohol sequentially and were finally cleaned with distilled water and dried. The lateral dimensions of the films were 6 and 1 cm and the source to substrate distance was 25 cm. The thicknesses of the films varied between 100 and 850 Å and were measured *in situ* using a quartz-crystal monitor. Before depositing the experimental PbSe film, thick (> 5000 Å) silver contact films (of breadth 2.5 cm) were predeposited at the ends of the glass plates so that they made large area contacts with the PbSe film when it was deposited. Preliminary measurements of resistance with applied voltage made with current flowing in opposite directions did not reveal any blocking barriers at the junctions.

The x-ray diffractograms of thin films of PbSe revealed that they were polycrystalline in nature, maintaining the same structure as that of the bulk PbSe. Figures 1(a) and

1(b), respectively, show the Debye-Scherrer photograph of the bulk PbSe alloy and the x-ray diffractogram of the typical PbSe thin film prepared in a vacuum of 5×10^{-5} Torr on glass substrate held at room temperature. Table I compares the d values of PbSe obtained from the powder photograph of Fig. 1(a) and the x-ray diffractogram of Fig. 1(b) with the standard d values of PbSe/Pb oxides obtained from the ASTM cards. Also compared are the relative intensities of reflections. It is found that both the d values and intensities match with the standard d values and intensities taken from the PbSe ASTM card, thus confirming that the bulk alloy and the thin films are of near-stoichiometric PbSe.

A second look at the x-ray diffractogram of Fig. 1(b) reveals an "amorphous" humplike peak centered around a 2θ value of about 30° . This amorphous hump arises because of the glass substrate used for preparing the films together with which the x-ray diffractogram of the films was taken. Figure 1(c) shows the x-ray diffractogram of the blank glass substrate which has a similar amorphous hump, confirming that the amorphous peak arises from the glass substrate.

However, there is one extra peak (sharp one) at a 2θ value of around 27° (with a d value of 3.31 \AA) which cannot be indexed by PbSe. There exists a high-pressure tetragonal phase labeled PbSe_2 at 70 kbar (ASTM card

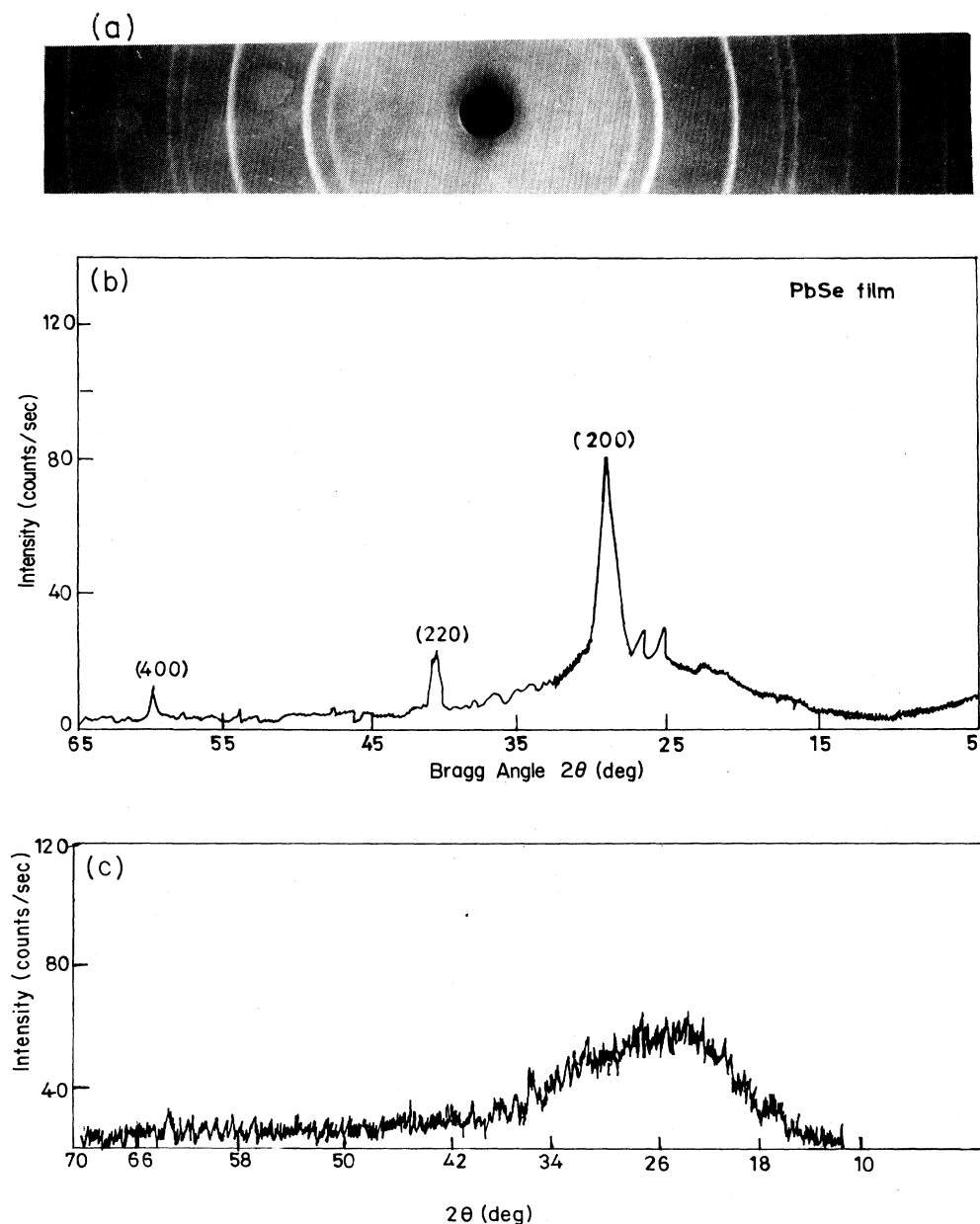


FIG. 1. (a) X-ray powder photograph of bulk PbSe alloy. (b) X-ray diffractogram of a typical PbSe thin film. (c) X-ray diffractogram of a blank glass substrate.

TABLE I. Comparison of d_{hkl} values of the PbSe bulk and PbSe thin film with the theoretical values of PbSe given in the ASTM Card No. 6-0354 and those of Pb_3O_4 oxide given in the ASTM Card No. 8-19. *W*, *ST*, *VST*, and *VVVW* denote weak, strong, very strong, and very very very weak, respectively.

d_{hkl} (theor.) (PbSe) (Å)	Intensity (theor.)	Observed d_{hkl}		Reflecting planes	d_{hkl}	Pb_3O_4 I/I_0	hkl
		Bulk (Å)	Thin film (Å)				
3.54	30	3.5275	3.562	(111)			
			3.372		3.38	100	211
3.06	100	3.0283	3.103	(200)			
			2.448		2.444	2	321
			2.363		2.289	12	222
2.165	70	2.1637	2.201	(220)			
			1.875		1.887	1	421
1.846	18	1.8416		(311)			
1.768	20	1.7588	1.674	(222)	1.689	2	422
			1.577		1.587	12	521
1.531	14	1.5304	1.542	(400)			
			1.513		1.5116	2	530
			1.452		1.4521	14	314
1.405	6	1.3969		(331)			611
1.369	25	1.3709		(420)			
1.250	16	1.2523		(422)			

No. 20-593), one of the d values of which is 3.22 Å.

However, as the difference between the observed d value and this is as much as 0.1 Å, it cannot be assigned to the high-temperature phase. Looking to the ASTM cards of oxides of Pb we find that there are several different oxides with different crystal structures, but there are two oxides which have d values close to the observed value. These are (1) Pb_3O_4 with d values of 3.38 and 3.28 Å and (2) $\text{PbO}_{1.57}$ with d values of 3.297 and 3.268 Å. These have I/I_0 ratios (I/I_0 is the relative intensity) of 100, 8, 20, and 20, respectively. Thus, we can conclude that this additional peak around a 2θ value of 27° arises from the lead oxide and most probably corresponds to the d value of 3.38 Å, which has $I/I_0 = 100$ and is very close to the observed d value. The existence of the oxide peak in the spectrum is quite understandable because the diffractogram is taken of the film which is exposed to atmosphere for a few days as it was stored in a dessicator after preparation. It may be added that the existence of the oxide peak in the diffractogram supports further our explanation of the change of electrical properties of the PbSe film on exposure to air as due to oxygen adsorption and interaction effects. Regarding the very minor high-angle ($2\theta > 40^\circ$) "peaks" observed it can be said that they are very shallow so as to merge with the noise in the diffraction spectrum and, hence, it is doubtful whether they are really peaks. In any case, these very shallow high-angle peaks can be indexed on one of the oxides, for example Pb_3O_4 , whose low-angle prominent peak has already been identified above. Thus, this further supports our contention of the interaction of oxygen with PbSe films leading to the observed changes in properties.

Once a film was deposited, it was taken out of the chamber by breaking the vacuum to mount the same on the conductivity setup described below. Any change in stoichiometry in the films will be the same for all the

films of different thicknesses studied because of the method of preparation employed and the precautions taken. Hence, the slight nonstoichiometry, if any, will be similar for all the films and hence is inconsequential. The conductivity setup¹³ consisted of a hollow copper cylinder brazed to a solid cylindrical disk of copper to the lower surface of which can be fixed a glass plate of size $2.5 \times 7.5 \times 0.2 \text{ cm}^3$ by means of a copper ring with bolts. The lower solid copper disk also contained a miniheater by means of which the copper disk and hence the glass plate serving as the substrate and hence the experimental film itself can be heated to elevated temperatures. The top hollow cylinder had brazed to it sturdy copper tubes through which liquid N_2 can be passed through the film substrate holder so that the film can be cooled below room temperature. The copper tubes also serve as supports to the *in situ* heater and/or cooler with substrate holder which is the conductivity setup. The copper tubes were brazed to a stainless-steel feedthrough which can be fitted to the base plate of the vacuum deposition unit. The feedthroughs served to take the liquid- N_2 -carrying tubes to the outside of the chamber and also serve as the base of the whole assembly which is vacuum-tight when fitted to the base plate of the deposition unit. By predepositing thick silver contact films at the ends of the glass substrates and taking electrical contacts through them and also from the heater and the copper-Constantan thermocouple serving as the temperature sensor to the outside by means of another vacuum-tight electrical feedthrough, it is possible to make electrical-conductivity measurements on the PbSe "*in situ*" immediately after formation without breaking the vacuum.

Leads were taken from the two ends of the silver films using pressure contacts. Once the film was mounted on the setup, the whole assembly was kept inside the chamber and later evacuated to a high vacuum of

5×10^{-5} Torr. A Gr Megohm bridge was used to measure the resistance of the film, as the resistance of the exposed films was quite high (10^5 – $10^6 \Omega$). The resistance values were noted as a function of temperature both during heating and cooling cycles in the temperature range 300–450 K.

To understand the effect of gas adsorption on PbSe films, conductivity of the as-grown films was also studied as a function of temperature *in situ*. As in the PbTe case,¹⁴ the resistance of the as-grown PbSe film was comparatively very low (1 k Ω) compared to its resistance after exposure to atmosphere. Therefore, a Wheatstone network was used to measure the resistance of the as-grown films as a function of temperature, *in situ*.

All the measurements were made in high vacuum (5×10^{-5} Torr) to avoid any unnecessary effects during the measurements.

III. RESULTS

Figure 2 shows the $\log_{10}R$ versus $1/T$ variation for a typical air-exposed film of PbSe of thickness 560 Å. We find that during the initial heating, the resistance increases with temperature but after some time reaches a maximum and then starts decreasing. However, this decrease is very short-lived since, immediately, a rise in resistance is observed with further increase in temperature. During cooling, the resistance monotonically in-

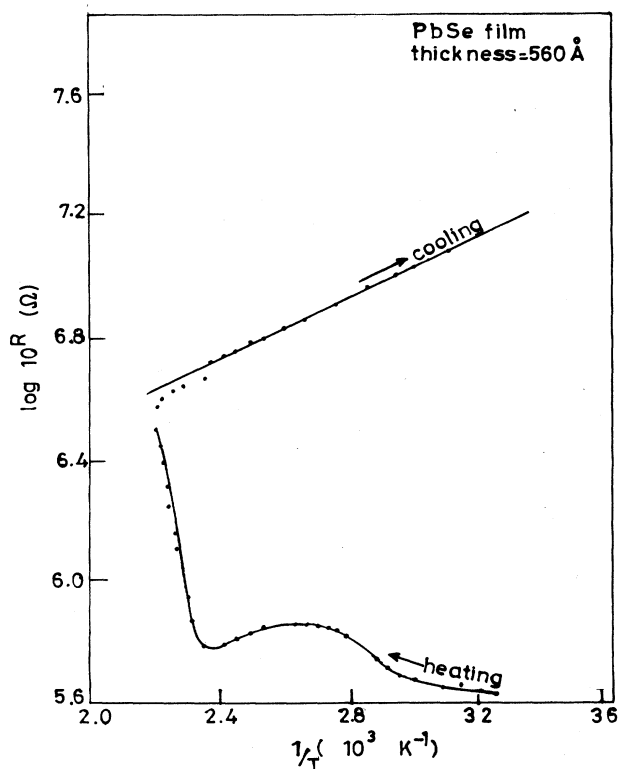


FIG. 2. Plot of $\log_{10}R$ vs $1/T$ for the PbSe thin film of thickness 560 Å during first heating and cooling after exposure to atmosphere.

creases with decreasing temperature and the $\log_{10}R$ versus $1/T$ plot is linear. The interesting observation, as seen in PbTe also,¹⁴ is that the cooling plot is above the heating plot.

Figure 3 shows the $\log_{10}R$ versus $1/T$ curves for the air-exposed PbSe films of thicknesses ranging from 100 to 850 Å during the first cooling cycle. The second and third cooling plots were found to be parallel to the first cooling curves and hence are not shown in the figure. We find that the $\log_{10}R$ versus $1/T$ plots are linear for all the films of various thicknesses, but their slopes are different. The activation energies calculated from their slopes vary from 0.25 to 0.5 eV. Figure 4 shows the dependence of the activation energy values E_i on the thickness of the films. No systematic variation of E_i with thickness is observed. However, it can be said (at least from the seven thicker films) that the activation energy depends nearly linearly on the reciprocal thickness, decreasing with decreasing thickness. However, the activation energy values of the three thinnest films are higher.

As the gas-adsorption effects severely influence the electrical properties of the Pb chalcogenides,^{14–17} the electrical resistivity measurements were also carried out on as-grown, unexposed thin films *in situ* to study the effect of adsorption of gases, mainly oxygen, when exposed to the atmosphere. Figure 5 shows the variation of the logarithm of resistance with reciprocal temperature of a typical as-grown unexposed lead selenide film of thickness 410 Å for two cycles of heating and cooling.

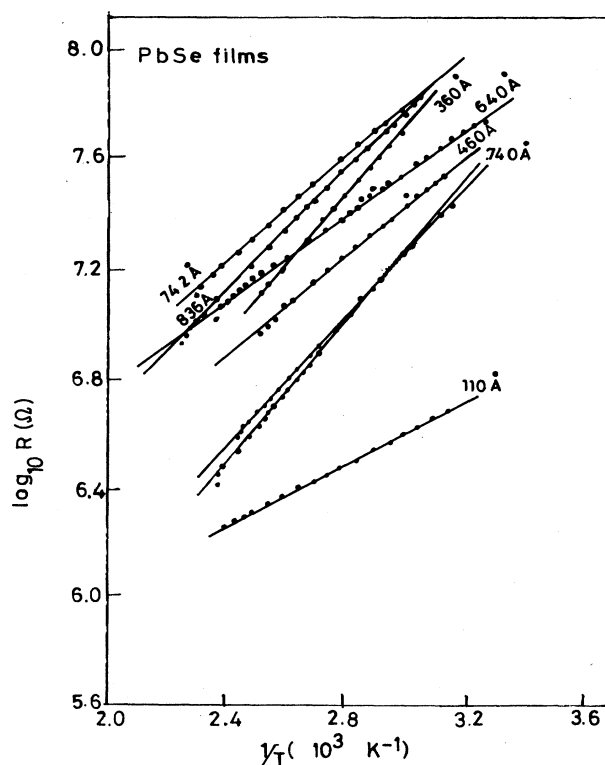


FIG. 3. Plots of $\log_{10}R$ vs $1/T$ for PbSe thin films of different thicknesses exposed to atmosphere.

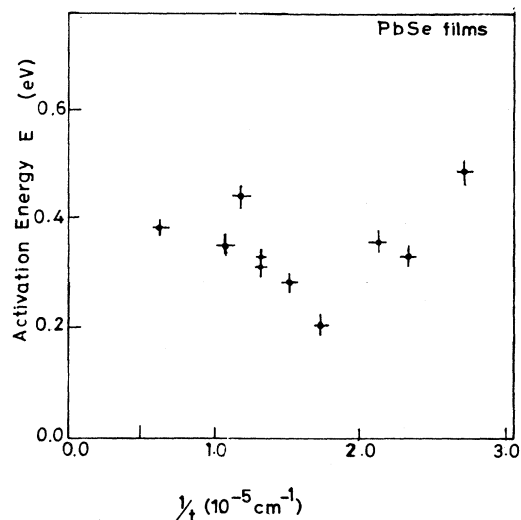


FIG. 4. Plot of activation energy E_i against inverse thickness of PbSe thin films.

Here too we find that the cooling curves lie above the heating curves. During heating, a nonuniform variation of resistance with temperature is observed. Figure 6 shows the $\log_{10} R$ versus $1/T$ plot for the above as-grown film of PbSe while cooling. We see that the plot is linear. The activation energy calculated from the slope is 0.28 eV.

Figure 7 shows the plot of the room-temperature resistivity ρ_F of as-grown PbSe films against the inverse of

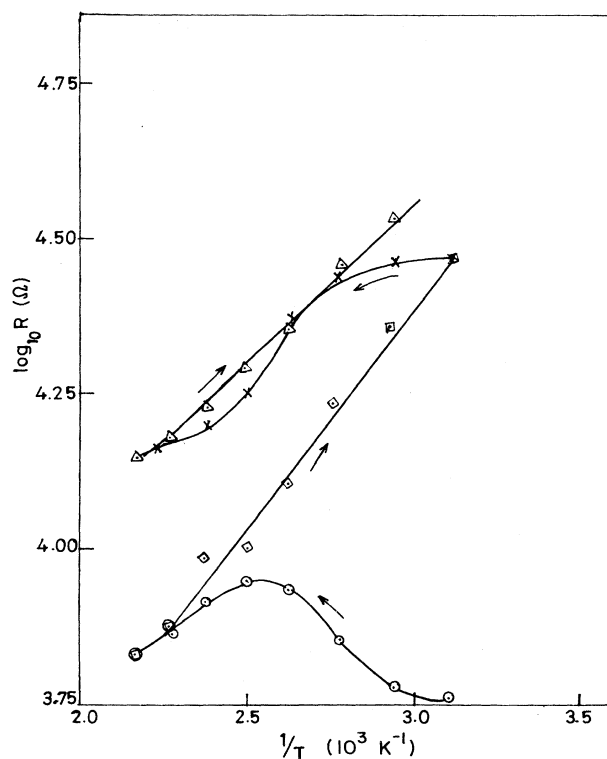


FIG. 5. Plot of $\log_{10} R$ vs $1/T$ of an unexposed (as-grown) thin film of PbSe during first heating and cooling.

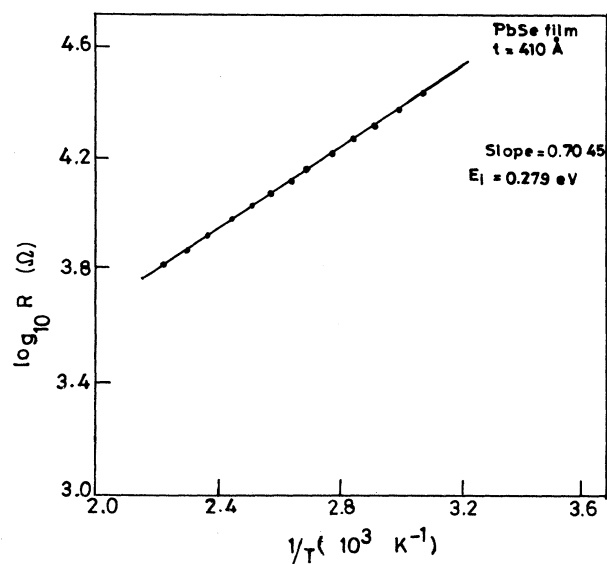


FIG. 6. Plot of $\log_{10} R$ vs $1/T$ of an unexposed (as-grown) thin film of PbSe.

thickness and we find that the plot is nearly linear, within experimental errors, with an intercept of $2.74 \times 10^{-3} \text{ } \Omega \text{ cm}$ and slope of $5.4 \times 10^{-8} \text{ } \Omega \text{ cm}^2$.

IV. DISCUSSION

A. Air-exposed thin films

Like PbTe, PbSe films are also nonstoichiometric in nature and their carrier concentration is quite high. The carrier concentration reported in thin films is found to be higher than that reported in bulk.⁹ A carrier concentration ranging from 10^{17} to 10^{18} cm^{-3} has been reported in thin films of PbSe.⁹ The energy gap of PbSe is 0.29 eV as reported in the literature.¹⁸ Many workers have reported the energy-gap values in thin films of PbSe too. However, the ambiguity whether the activation energy values from the slope of $\log_{10} R$ versus $1/T$ curves should be

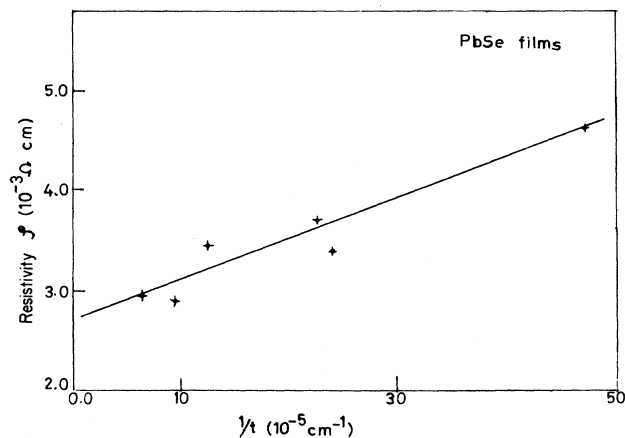


FIG. 7. Plot of resistivity vs inverse thickness of unexposed (as-grown) PbSe thin films.

called the energy gap still persists. This is because the electrical properties of polycrystalline films exposed to atmosphere are completely affected by the barriers at the grain boundaries and adsorption effects.

The initial slow rise in resistance of PbSe films with temperature suggests that the carrier concentration is almost constant, but the mobility decreases due to scattering at the lattice vibrations. This is possible if the system is degenerate and the intrinsic conduction is yet to start. However, whether the system is in the intrinsic range or in the extrinsic range will be decided by the temperature and the carrier concentration. But the Hall effect measurements could not be done due to experimental limitations in the laboratory. However, during cooling, we observe a single straight line in the $\log_{10}R$ versus $1/T$ plots in the temperature range 300–460 K. Secondly, the activation energy values calculated for the slopes of the above straight lines are comparable with the energy gap of PbSe. This suggests that the PbSe films are intrinsic even at room temperature. Hence, the above explanation for the initial increase of resistance is only tentative.

The decrease of resistance after the initial increase can be attributed to the intrinsic conduction, as has been done for PbTe.¹⁴ The sharp increase in resistance observed at high temperatures (>450 K) is attributed to a sharp decrease in mobility due to creation of defects at elevated temperature, as proposed by Smith¹⁹ and later confirmed by Newman²⁰ and Miller *et al.*²¹ among others.

The slow decrease of resistance during the first heating and a relatively sharper increase in resistance at high temperature can be explained as follows. Apparently there can be three processes taking place in air-exposed PbSe films during heating: (i) intrinsic conduction, (ii) desorption of oxygen, and (iii) creation of thermally generated defects, particularly at high temperatures. However, intrinsic conduction at room temperature is debatable since it depends upon the carrier concentration in the material. However, we observe a single straight line in the $\log_{10}R$ versus $1/T$ plot in the temperature range 300–540 K, and the activation energy values are comparable with the energy gap of PbSe. Hence, the decrease of resistance during the initial heating may be attributed to the intrinsic conduction taking place in PbSe films. But at higher temperatures (>450 K) the resistance increases steeply. This makes us believe that some other mechanism, other than intrinsic conduction, is responsible for this. This mechanism can be the desorption of oxygen. The desorption of oxygen from the film surface decreases the carrier concentration in a “*p*”-type sample and thus increases the resistance of the sample. (Oxygen is a *p*-type dopant in Pb chalcogenides.) Since the films were exposed to atmosphere before mounting them in the conductivity setup, a lot of oxygen atoms and/or molecules will have been adsorbed at the surface of the film. At high temperatures, oxygen atoms get desorbed and this also increases the resistance of the films. The third mechanism proposed by Smith²⁰ can also be responsible for the increase of resistance at high temperatures. It was argued that in chalcogenides, defects will be created at high temperatures. These defects can act as scattering

centers for the carriers, thereby appreciably bringing down the mobility of the carriers. This results in a sharp increase in resistance of the film. Thus, due to both the above mechanisms, the resistance of the films can increase sharply at high temperatures.

During cooling, we observe a monotonous increase of resistance with decreasing temperature, thus exhibiting the semiconducting behavior. This is because of the hysteretic nature of the thermal defects generated at high temperatures. These defects exhibit hysteresis, i.e., the defects created during heating are not eliminated immediately during cooling, but only after some time. Similarly, the desorbed gas molecules will not be immediately adsorbed during cooling, as continuous pumping out of air is done in the vacuum chamber. This duration of hysteresis is quite long (about 20–24 h) and hence during cooling, only the thermal activation is responsible for the conductivity changes as the extent of adsorbed gases remains independent of temperature.

The slopes of the $\log_{10}R$ versus $1/T$ plots for PbSe films of different thicknesses give the activation energy values in the range 0.25–0.5 eV. These values are, of course, comparable with the energy gap of PbSe, though variation of these values is found from film to film. A systematic variation of these activation energy values with thickness is absent and hence these abnormal values should be attributed to the varying deposition parameters like vacuum, deposition rate, etc. However, the deposition parameters were essentially the same in all the evaporations. However, exactly identical conditions are only ideal and not practicable. Further, the electrical conductivity of the air-exposed films does not show any systematic variation with thickness.

B. Unexposed (as-grown) thin films

In order to eliminate the effects of gas adsorption in PbSe films and to confirm the creation of defects at high temperature, as mentioned earlier, *in situ* conductivity studies were also carried out on as-grown films of PbSe as shown in Fig. 5. Here too, we find that the cooling cycles are above the heating cycles. This confirms that at high temperatures, in addition to oxygen desorption, another mechanism is also taking place in the system. The hysteresis was observed here also: When, after the first cooling of the as-grown films, they were kept in vacuum for a day or two, the resistance was found to slowly decrease to its original as-grown value. The activation energy calculated from the slope of the $\log_{10}R$ versus $1/T$ plot for the cooling cycles (Fig. 6) was found to be 0.28 eV.

The thickness dependence of the conductivity of the as-grown (unexposed) films at room temperature is shown in Fig. 7. We find that the conductivity varies nearly linearly with the inverse of thickness. As mentioned before, the conductivity of air-exposed (and heated) films did not show any systematic dependence, let alone linear dependence, on reciprocal thickness, unlike the conductivity of the unexposed films. This is surely because of the fact that the conductivity of the air-exposed films is completely dominated by gas-adsorption (oxygen-adsorption) effects and hence size-effect dependence is

completely masked by them. This conclusion is unmistakable from the observations made by us of the effect of gas adsorption on PbSe thin-film conductivity both in the present work and also in the earlier work.¹⁷

The linear dependence of the film conductivity with reciprocal thickness observed in Fig. 7 arises due to the size effects influencing the film conductivity and can be explained by a suitable size-dependent film conduction model like the effective mean free path model.¹²

In polycrystalline thin films, in addition to the usual lattice and defect scattering, other scatterings come into picture. The scattering at the film surfaces and that at the grain-boundary surfaces significantly contribute to the resistivity, especially when the bulk electron mean free path is large and comparable with the thickness of the film or the grain size. Hence, when dealing with thin films, the surface scattering effects should be taken into account.

The dependence of resistivity or any other transport parameter on the thickness of the film is referred to as the "size effect" or the dimensional effect. The size-effect studies are very interesting, since these would enable us to determine the mean free path, the carrier concentration, and the Fermi surface area, which are some of the important parameters of conduction. Fuchs²² and later Sondheimer²³ worked out the size effect in the case of thin films, taking into account the scattering from the two external surfaces. However, they did not take into account scattering from the grain-boundary surfaces.

Hence, the Fuchs-Sondheimer theory can be used only for single-crystal films and not for polycrystalline films. Mayadas and Shatzkes^{24,25} proposed a conduction model for polycrystalline films that takes into account the impurity and lattice scattering, the surface scattering, and the grain-boundary scattering. They assumed that the grain boundaries could be represented by arrays of planes whose scattering effects are described by Dirac potentials; they further assumed that the planes parallel to the electric field do not have any influence on the electronic conductivity of the film. Only the planes perpendicular to the field contribute to the scattering. The average scatterer spacing d was identified as the grain diameter D . When the surface scattering is also taken into account, the expression derived for resistivity of the film by Mayadas and Shatzkes is quite complicated.

As the size-effect expression obtained by the Mayadas-Shatzkes model is quite complicated, many others^{26,27} tried to obtain simplified expressions for the size effects in polycrystalline films. Recently, Tellier¹² has successfully proposed a model, namely the effective mean free path model, wherein the size-effect expression is quite simple and similar to the Fuchs-Sondheimer function. She described the grain-boundary scattering by defining a relaxation time τ_g such that $l_g = \tau_g v$, where l_g is the effective mean free path in an infinitely thick film and v is the carrier velocity.

Tellier then arrived at an asymptotic equation for the film conductivity by replacing l_B by l_g and σ_B by σ_g in the expression for σ_F arrived at by the Fuchs-Sondheimer model.

Thus, we can write, according to Tellier's model,

$$\sigma_F = \sigma_g \left[1 - \frac{3}{8} \frac{1-p}{k_g} \right]$$

or

$$\rho_F = \rho_g \left[1 + \frac{3}{8} \frac{1-p}{k_g} \right], \text{ for } k_g > 1$$

where $k_g = t/l_g$ is called the reduced thickness of the polycrystalline film and p is called the specularity parameter giving the fraction of electrons incident on the surface that are specularly scattered. Other symbols have their usual meaning.

Hence, if we plot a graph of ρ_F versus $1/T$, the intercept will give us the value of ρ_g , the grain-boundary resistivity, and the slope $= \frac{3}{8} l_g (1-p) \rho_g$. If we know the value of l_g , we can calculate the specularity parameter p and vice versa.

From Fig. 7, the intercept $\rho_g = 2.74 \times 10^{-3} \Omega \text{ cm}$, and the slope of the plot is $5.4 \times 10^{-8} \Omega \text{ cm}^2$. Taking the bulk value of conductivity of PbSe, $\sigma_B = 1/\rho_B = 1.25 \times 10^2 (\Omega \text{ cm})^{-1}$,²⁸ and the bulk mean free path, $l_B = 200 \text{ \AA}$,²⁹ and using the relation $l_g = l_B \sigma_g / \sigma_B$ the grain-boundary mean free path l_g is evaluated as 580 \AA . Using this value of the mean free path in the expression for the slope, we can calculate the specularity parameter p as 0.9.

The value of p suggests that most of the carriers are specularly scattered. From the thermoelectric power studies of PbSe films, we found that the specularity parameter p (Ref. 30) was equal to 1. However, from the resistivity data we find that p is not equal to 1 but very near to 1. This slight change is explainable because the thermoelectric studies were done on air-exposed films of PbSe whereas the resistivity studies were conducted *in situ*, without exposing the films to atmosphere. Hence, we find that the gas adsorption not only alters the conductivity of the PbSe films, but also the surface scattering mechanism.

V. CONCLUSIONS

(1) During the initial heating, a slow increase of resistance was observed followed by a slow decrease in the case of PbSe films. But at temperatures $> 450 \text{ K}$, a sharp rise in resistance was observed. This was attributed to the formation of thermally generated defects at high temperatures, which decreases the mobility drastically. The cooling cycles were found to be always above the respective heating cycles.

(2) On cooling, semiconducting behavior was observed and the $\log_{10} R$ versus $1/T$ plots were found to be linear. The activation energy values calculated from the slopes of these cooling plots were found to be comparable with the energy gap of PbSe.

(3) The *in situ* conductivity measurements confirmed the defect creation at high temperatures and also their hysteresis behavior. Here also, the cooling cycles were above the respective heating cycles.

(4) Though the activation energy values varied with the thickness of the film, no systematic variation of E_i was

observed. Hence it was concluded that the activation energies were independent of thickness.

(5) The conductivities of the as-grown films of PbSe obeyed Tellier's effective mean free path model and the ρ_F versus $1/T$ plot was found to be linear.

(6) As in PbTe films, the scattering process taking place at the surface of the as-grown PbSe films was found to be

different from that of the exposed films.

The p values calculated from the thermoelectric power studies of air-exposed films and conductivity studies of as-grown films of PbSe were found to be slightly different. This implies that the gas adsorption not only affects the carrier concentration in films, but also affects the surface scattering mechanism.

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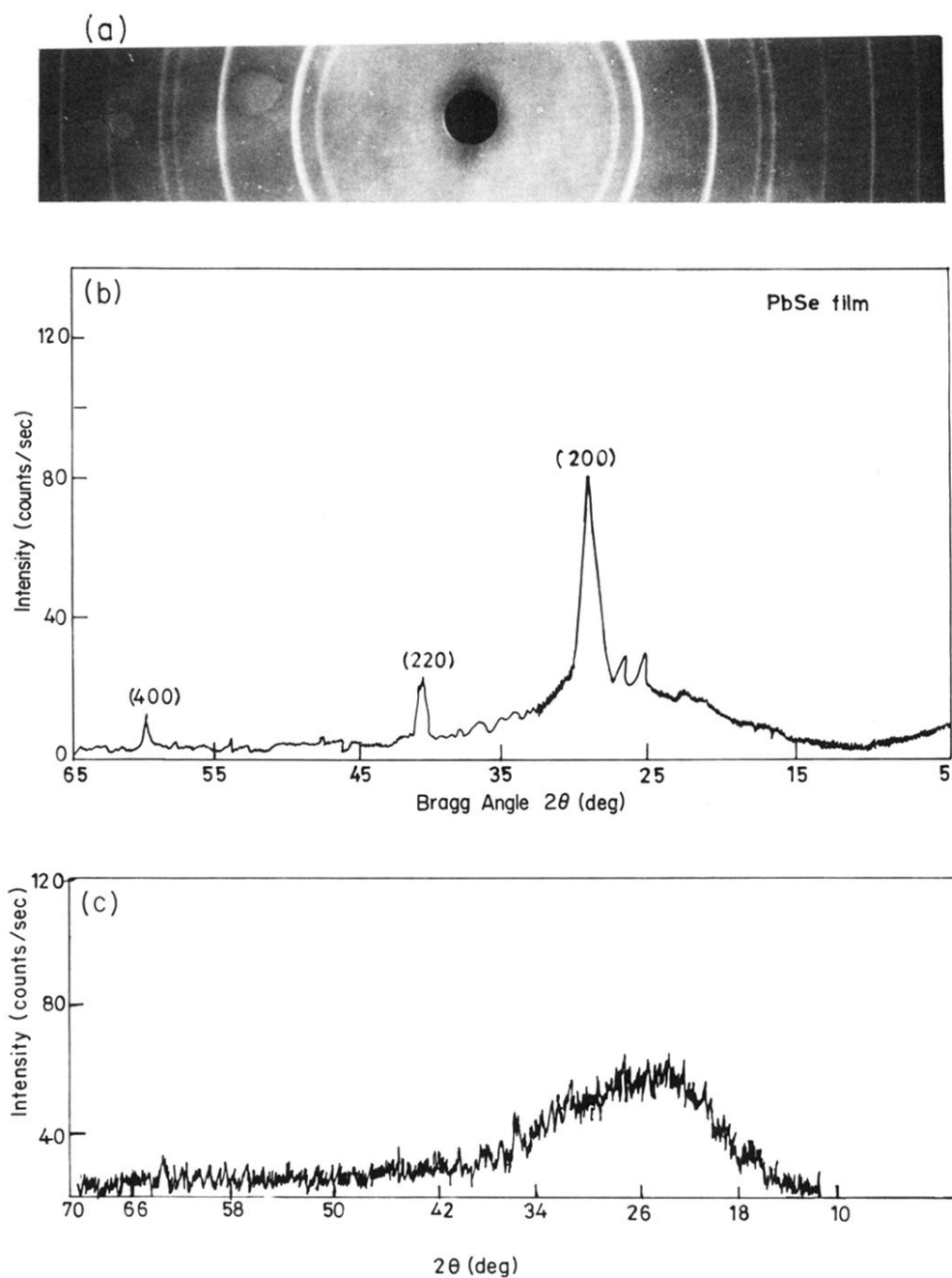


FIG. 1. (a) X-ray powder photograph of bulk PbSe alloy. (b) X-ray diffractogram of a typical PbSe thin film. (c) X-ray diffractogram of a blank glass substrate.